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AN INVESTIGATION OF PREFERENTIAL INTERFACIAL REACTIONS IN NONMETALIZED COMPOSITE SOLID PROPELLANT COMBUSTION

by

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13. ABSTRACT

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Preferential interfacial reactions did not exist in the propellants studied at the pressures and accelerations at which the investigation was made. Soft binders in nonmetalized propellants were found to allow oxidizer-binder interaction at high accelerations resulting in unstable combustion and self-extinguishment. Nonmetalized composite propellants that did not contain opacifiers appeared to to burn more erratically in a positive acceleration environment.

An Investigation of Preferential Interfacial Reactions in Nonmetalized Composite Solid Propellant Combustion

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SYMBOLS AND ABBREVATIONS

G - Acceleration divided by gravitational constant.

PBAA - Polybutidiene-acrylic acid

PBAN - Polybutidiene-acrylic Acid-acrylonitrile

PIR - Preferential Interfacial Reactions

$\dot{r}_o$ - Base burning rate at static conditions

$\dot{r}$ - Burning rate

$\frac{\dot{r}}{\dot{r}_o}$ - Augmentation

I. INTRODUCTION

Metalized and nonmetalized composite solid propellants exhibit a significantly higher burning rate in an acceleration environment than in a static (zero g) condition. To optimize motor design of spin stabilized rockets and other solid propellant vehicles expected to operate in acceleration environments, burning rate sensitivity must be characterized. Several experimental and analytical investigations have been conducted in recent years in an attempt to analyze and model this phenomenon. Two analytical models for nonmetalized propellants have resulted.

Glick [1] in 1966 expanded on Summerfield's [2] granular diffusion flame model to include acceleration effects. The model postulated that augmentation resulted primarily from the effects of acceleration forces on the gas phase reaction. The model failed to adequately explain nonmetalized augmentation phenomena as discussed in the literature [3,4].

Sturm [5] in 1968 proposed a model to explain acceleration sensitivity of nonmetalized composite propellants. This model was an extension of Fenn's [6] preferential interfacial reaction model for static burning.

Fenn's model assumed that a premixed "phalanx" flame region existed on the interface between the fuel and oxidizer in a propellant (Fig. 1). This flame formed a spearhead of hot reaction gases resulting in a higher burning rate along the

interface than the overall mass burning rate of the propellant. The phalanx flame might proceed around an oxidizer particle prior to its consumption resulting in the particle being freed from the fuel matrix by a gas film (Fig. 2a). If the particle were small enough, it would be carried away by aerodynamic drag forces caused by the evolving gases (Fig. 2b). This would lead to oxidizer depletion on the surface. The overall burning rate of the propellant would thus be less than optimum due to loss of potential heat for further fuel pyrolysis.

Sturm proposed that these oxidizer particles were responsible for augmentation in an acceleration environment. When acceleration forces directed normal and into the burning surface (+g) acted on fine particles normally carried away in a static environment, they would counteract the drag forces acting on the freed particles. If the body forces were greater than the drag forces, the oxidizer particle would continue to be held on the surface until it burned to a small enough size to be carried away (Fig. 3a). This would result in more oxidizer being available and would provide greater heat transfer and thus a higher burning rate. If the body forces were less than the drag forces, the particle would continue to be carried away (Fig. 3b). At some maximum acceleration field all oxidizer would be held on the surface and the peak burning rate would have been attained.

The model assumed that no appreciable consumption of the oxidizer took place prior to it being freed. Coarse particles

in the oxidizer blend were not considered to contribute to the augmentation mechanism. Negative acceleration field burning was assumed to have the same characteristics as static conditions.

Although Sturm's physical model can be used to explain most observed augmentation phenomena, recent investigations indicate that the existence of preferential interfacial reactions is questionable. Hightower and Price [7] through quench studies and scanning electron microscope examination have found no evidence of subsurface reactions. Cowles and Netzer [8] found a burning rate augmentation greater than 1.0 for acceleration directed normal to and out of the burning surface (negative g). It was the purpose of this investigation, in light of the inconsistencies noted, to determine if preferential interfacial reactions do exist as an augmentation mechanism.

II. METHOD OF INVESTIGATION

To investigate the presence of preferential interfacial reactions, four nonmetalized solid propellants were selected. Each had different oxidizer (ammonium perchlorate) size distribution but similar binder characteristics. Propellant designations and properties are given in Table I. Each propellant was tested in both an unstressed (as cast) and a previously stressed (dewetted) condition. Propellant strands were burned in positive, negative and static (zero g) acceleration fields as indicated in Table I.

As a propellant was loaded beyond a certain critical stress, bonds in the region of the interface between the oxidizer particle and the binder were broken, and the binder pulled away from the particle. This resulted in vacuoles, or voids, forming along the uniaxial tensile axis of the large oxidizer particle (Fig. 4). Once the stress was removed, the voids collapsed leaving the bonds broken at the interface. The particles remained in this condition for a finite period of time. Thus, a change in the interfacial characteristics between the large oxidizer particles and the binder was obtained by stressing the propellant.

Comparison of the burning rates of each propellant with only the interfacial characteristics modified was then made to determine if preferential interfacial reactions existed.

III. EXPERIMENTAL PROCEDURES

This investigation was conducted at the Naval Postgraduate School Rocket Test Facility. A combustion bomb mounted on a three-foot radius centrifuge was utilized in all tests. Further details of the centrifuge and test facility may be found in references 9 and 10.

Propellant strands utilized in all tests were 1/2 in. by 1/2 in. in cross section and 2 in. long. They were rigidly inhibited on all but the normal or burning face by Selectron 5119 resin. A small amount of black powder and glue mixture was placed on the burning face, and a nichrome resistance wire was placed adjacent to the burning face. Electrical current heated the nichrome wire, igniting the black powder, which in turn initiated propellant burning. All tests were made at 500 psi mean pressure and constant centrifuge speed during the burning process.

Dewetting characteristics of the propellants were obtained utilizing a dilatometer and in Instron tensile testing machine.

The dilatometer consisted of a test cavity filled with silicon oil. It was instrumented to measure stress, strain and volume change of the propellant sample undergo load. Detailed explanation of the dilatometer and operating procedures may be found in Ref. 11. Specimens 1/2 in. by 1/2 in. in cross section and 4 in. in length were tested in

the dilatometer. Specimens were loaded at a constant strain rate to determine stress and strain required before the onset of dewetting.[1]

Once the required stress for onset of dewetting had been obtained, specimens of the same size were loaded on the Instron tester at the same strain rate to a stress level intermediate between onset of dewetting and failure. After loading and unloading, the specimens were immediately reloaded to verify dewetted stress-strain plots as reported in Ref. 12.

Twenty four hours were required to inhibit and burn propellant strands. Therefore, selected samples of each propellant were retested on the Instron after this period of time to insure that they retained dewetted properties.

[1]LCDR J. E. Wood, USN assisted in obtaining dewetting data for propellant B-1

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. DEWETTING CHARACTERISTICS

Figures 5, 6 and 7 show dilatation (ratio of volume change to original volume) for propellants B-1, B-2 and N-3. N-1 propellant data are not presented since no dewetting was evident prior to sample fracture.

No vacuole formation will occur prior to onset of dewetting, and since propellants are typically incompressible, dilatation will be essentially zero until dewetting occurs. At the critical stress for dewetting, dilatation versus stress or strain will become nonlinear. This nonlinearity will continue until no more void formation occurs. From this point dilatation will become linear with increasing stress. Figure 5 indicates that propellant B-1 dewetted at approximately 25 psi. Figure 6 indicates that propellant B-2 dewetted at approximately 45 psi. The N-3 propellant was observed to dewet almost instantaneously due to large oxidizer particle size (Fig. 7).

Figures 8, 9 and 10 show the stress-strain curves resulting from tensile testing. All propellants exhibited characteristic dewetted stress-strain relations [12] on immediate reload and retained their dewetted characteristics after a twenty four hour period as indicated by similar curves of 24 hour reload.

B. EFFECT OF ACCELERATION ON PROPELLANT B-1

Burning rate data obtained for propellant B-1 in positive and negative acceleration fields are presented in Fig. 11. The base burning rate ($\dot{r}_o$) and augmentation of both the stressed and unstressed propellant were essentially the same. Augmentation obtained at negative 1000g was 0.92 in both the stressed and unstressed condition. Considerable data scatter was encountered in a high positive acceleration environment while negative acceleration data scatter was negligible. The Langley Research Center (LRC) data point was taken from Ref. 13. This was based on the same propellant but burned as a fifteen square-inch slab with a two-inch web thickness. Northam [13] noted upon extinguishment of B-1 propellant slabs that severe pitting had taken place. Small particles of unidentified material (possibly carbon or tricalcium phosphate additives) were found in many pits. The pits observed by Northam were of the size of the cross section utilized in the present investigation.

The reason for the significantly higher augmentation obtained in Northam's investigation may be concluded to be due to large scale effects of surface accumulation and pitting. The resulting increased surface area gave a larger burning surface and thus a greater burning rate than that observed in small strand samples.

Data scatter observed in this investigation may be due to surface accumulation in some tests. However, no positive acceleration tests yielded negligible augmentation. Therefore

surface accumulations and pitting cannot completely account for the augmentation observed for this propellant.

C. EFFECT OF ACCELERATION ON PROPELLANT B-2

Figure 12 presents the burning rate augmentation data obtained with the B-2 propellant for both the stressed and unstressed conditions. Base burning rates were essentially the same for the stressed and unstressed propellant. Augmentation at negative accelerations was slightly lower for the unstressed propellant. High negative acceleration produced no augmentation for the stressed propellant while a five percent augmentation resulted for the negative 50g acceleration field.

Considerable data scatter was present in the positive g environments. Fast burns were especially prevalent for the stressed propellant at 50 and 250g. Negative acceleration data showed very little scatter.

Stressed propellant scatter may have been due to internal fracture of the propellant. This propellant was stressed very close to fracture to attain dewetting. Data scatter could also have been caused by inhomogenuity of the propellant mix. Propellant B-2 was made in a small batch with the possibility of settling of the oxidizer particles during curing.

D. EFFECT OF ACCELERATION ON PROPELLANT N-3

Augmentation data for propellant N-3 in both the stressed and unstressed condition are presented in Fig. 13. Base burning rates and augmentation were essentially the same for both stressed and unstressed propellants. Augmentation at

negative accelerations was negligible. Data scatter was prevalent in the stressed propellant in a positive acceleration field. This scatter may also have been due to small batch size and internal fracture.

Both propellant B-2 (AP/PBAA) and the N-3 (AP/PBAN) propellant were somewhat translucent and did not contain any additives (carbon, etc.) to prevent radiative heat transfer below the surface during combustion. Substantial subsurface heating may have been occuring which could have softened or altered the binder characteristics. The positive acceleration environments may then have produced varied effects upon the propellant, yielding the observed data scatter. Burning rate data scatter in acceleration environments are typically greater for nonmetalized propellants that do not contain opacifiers than for nonmetalized propellants that include such additives or for metalized composite propellants [3, 5, 14, etc.].

E. APPLICABILITY OF THE PREFERENTIAL INTERFACIAL REACTION MODEL

Table II presents a summary of general trends noted for each propellant tested.

Base burning rate was essentially unchanged for all propellants when dewetted. For the preferential interfacial reaction model (PIR) to explain this observed base burning rate data, one of the following arguments could be made:

1. No dewetting had occurred in the propellants when stressed.

2. Large oxidizer particles dewetted in the stressed state had no effect on the base burning rate.

3. Large dewetted oxidizer particles were "blown" off the surface in a zero g condition. However, a burnable pit was left by the oxidizer particle. The increased burning area of the pit offset the energy lost by the oxidizer depletion, resulting in no appreciable burning rate change.

It is unlikely that no dewetting occurred since considerable data support the presence of dewetting in all the stressed propellants.

The positive acceleration data were meaningful for propellant B-1. However, data scatter was too great for propellants B-2 and N-3 to consider these data in more than a qualitative manner. The augmentation obtained for the dewetted B-1 propellant did not change significantly from the as-cast data. Either argument two or three above could be used to explain this observation in light of the PIR model.

It should be noted that the positive acceleration data for propellant N-3 are inconsistent with Sturm's original model [5]. The original model assumed large oxidizer particles did not contribute to burning rate augmentation. Propellant N-3 consisted of a narrow blend (420-500 micron) of large oxidizer particles. Yet, this propellant exhibited burning rate augmentation in both the stressed and unstressed condition.

Assuming preferential interfacial reactions do exist, no augmentation should have resulted in a negative g acceleration field unless physical extraction of the oxidizer particles had taken place. If oxidizer particles were extracted, the burning rate may have increased, decreased or remained the same as the base burning rate. This would be dependent on the condition of the pit remaining after particle extraction. If the resultant pit was combustible, the burning rate could increase due to increased burning area. If the pit was combustible and burning area of the pits off-set the depletion of oxidizer, no change in the burning rate would result. If the pit was inert (fuel rich), and the burning rate would decrease due to oxidizer depletion.

All propellants tested exhibited a decrease in burning rate in the unstressed state at all negative accelerations. The data were most pronounced for propellant B-1. If preferential interfacial reactions were to explain this phenomenon, physical extraction of oxidizer particles had to have taken place. The resulting pits left by the extracted particles had to be inert or the oxidizer lost to combustion had a greater effect than the increased active surface area. Operating on this assumption, stressing the propellants should have resulted in more large oxidizer particles being extracted and a larger decrease in burning rate. However, the stressed B-1 propellant had the same augmentation at negative 1000g as the unstressed propellant. This is an inconsistency with the model.

The data for propellant B-2 (Fig. 12) show an increase in burning rate for the stressed propellant at negative accelerations. For this to have occurred within the framework of the PIR model, pits remaining after oxidizer extraction had to be burnable and had to more than compensate for the oxidizer lost to combustion. This contradicts the assumptions made to justify the unstressed propellant data and is another inconsistency not readily explained by the model.

The N-3 data further verify the model inconsistencies found for propellant B-2.

F. BURNING INSTABILITIES

The propellants that had soft binders (B-2 and N-3) exhibited burning instabilities and self extinguishment in high positive acceleration fields (Table II). Post-fire propellant residue remaining in the casings was subsequently burned in an atmospheric environment after removal from the case. This burning instability implied that some physical interaction of the binder and oxidizer was occurring at the higher positive accelerations. Possibly the oxidizer particles were forced down into the soft binder, causing partial or complete extinguishment. This suggests a possible augmentation mechanism for these propellants.

V. CONCLUSIONS

Inconsistencies between the basic assumption of preferential interfacial reactions in Sturm's model and observed phenomena coupled with previous evidence [7,8] leads to the conclusion that preferential interfacial reactions are not responsible for the burning rate acceleration sensitivity of nonmetalized AP/PBAA composite propellants. Significant preferential interfacial reactions did not exist for the propellants investigated at the pressures and acceleration levels tested.

Any solid material additive (carbon, tricalcium phosphate, or impurity) may result in pitting and burning rate augmentation in an acceleration environment but an additional unknown mechanism(s) is also present which results in augmentation.

Propellants with soft binders burn unstably in a high acceleration field. This may be due to physical interactions of the oxidizer and binder and may be the augmentation mechanism for these propellants.

Nonmetalized composite propellants that do not incorporate opacifiers to prevent subsurface heating appear to burn more erratically in positive acceleration environments.

Table I. Propellant Designations and Properties

Propellant	Binder		Ammonium	Perchlorate		Additives	Binder Characteristics	Acceleration Field	
	type	wt. %	mix	size	wt. %			+g	-g
B-1	PBAA	14.5	Bimodal	26 188	28.5 56.6	Carbon TCP	firm	0-1000	1000
B-2	PBAA	25	Bimodal	18 200	56.25 18.75	TCP	soft	0-1000	50 1000
N-3	PBAN	21	Unimodal	420	79.0	none	soft	0-250	250
N-1	PBAN	21	Unimodal	9	79.0	none	soft		

Table II. Summary of Experimental Results

Propellant	r_o stressed versus r_o unstressed	Positive g comparison	Negative g Augmentation, unstressed	Negative g Augmentation, stressed	Burn instabilities	Postfire residue in rigid inhibitor
B-1	no change	Stressed had slightly greater augmentation	0.93 @ -1000g	0.93 @ -1000g	minor	none
B-2	no change	Stressed had slightly greater augmentation	0.96 @ -50g 0.95 @ -1000g	1.05 @ -50g 0.99 @ -1000g	Slow starts, erratic burns, partial extinguishment 250-1000	Unburned propellant 500 - 1000g
N-3	no change	Stressed had slightly greater augmentation	0.98 @ -250g	1.00 @ -250g	Slow starts, partial extinguishment 100-250g. No burn above 250g.	Unburned propellant 250g

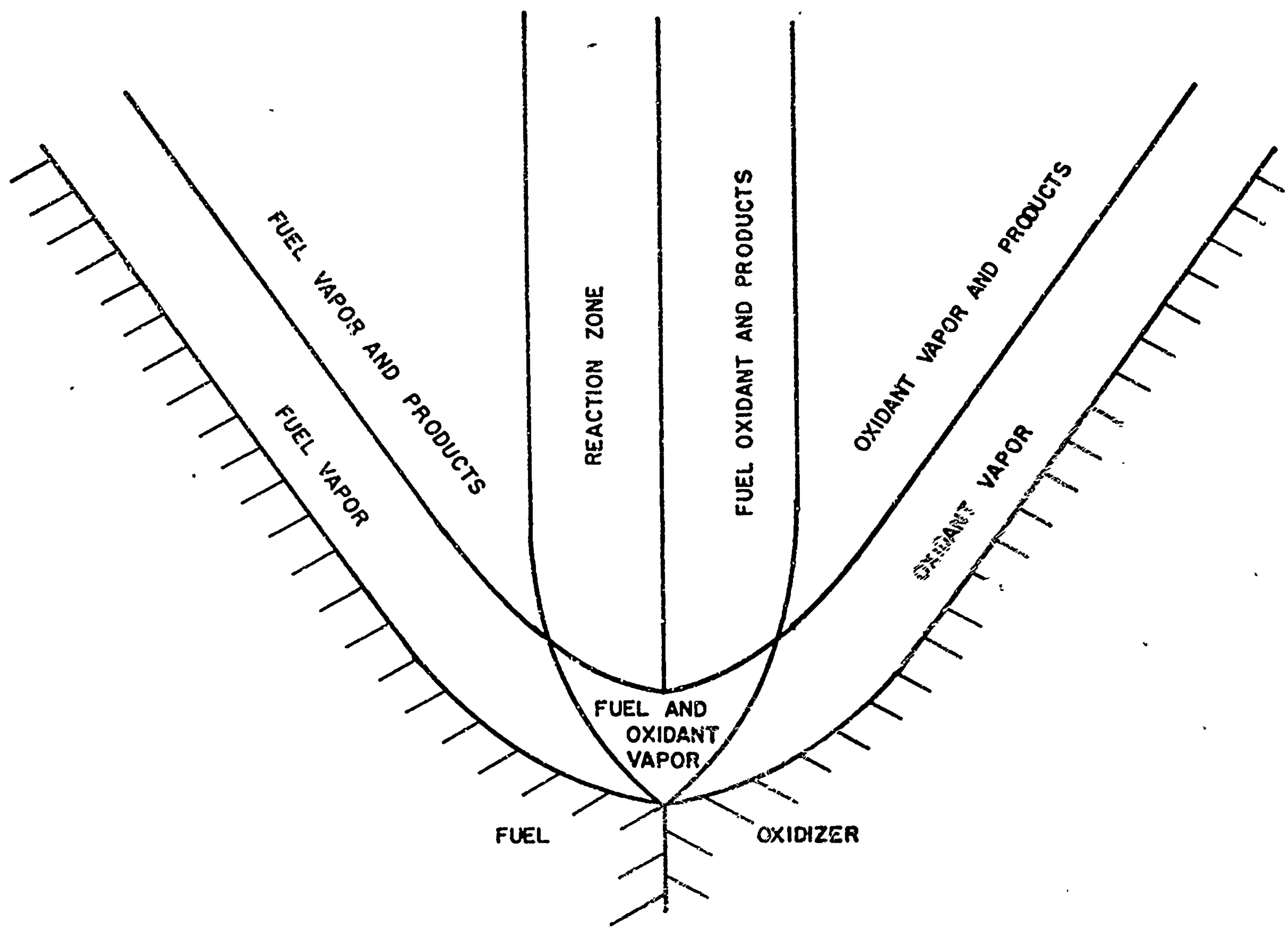
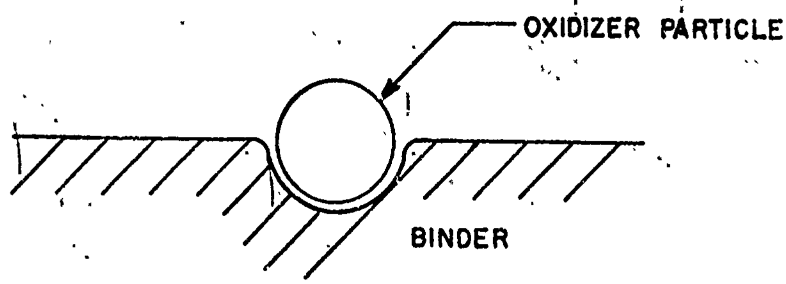
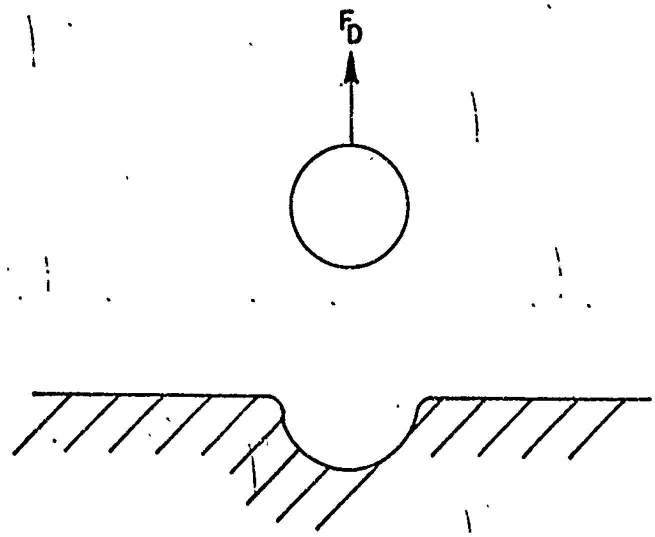


Figure 1. Phalanx Flame at Steady State (taken from Ref. 6)

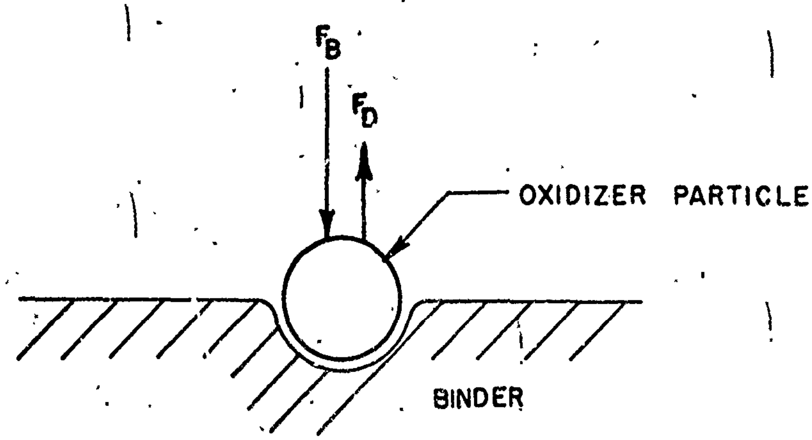


(a) Oxidzer particle free on gas film

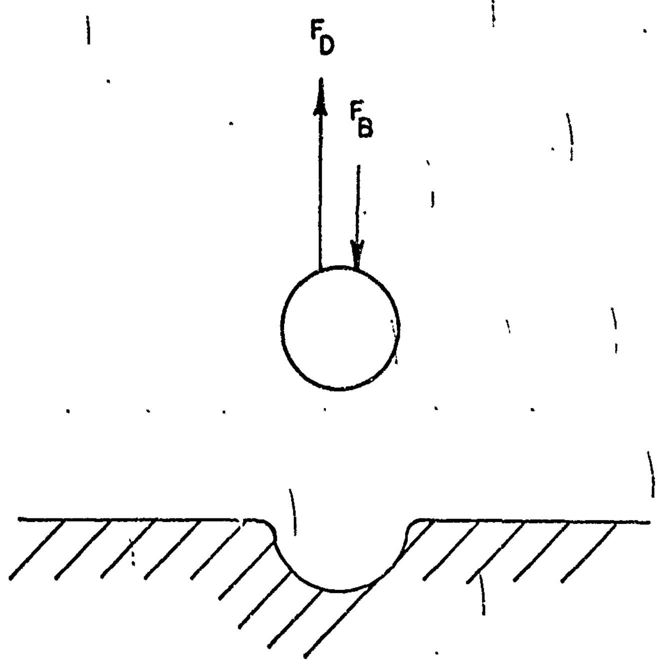


(b) Oxidizer particle carried away by aerodynamic drag forces

Figure 2. Fenn's Model for Static Conditions.

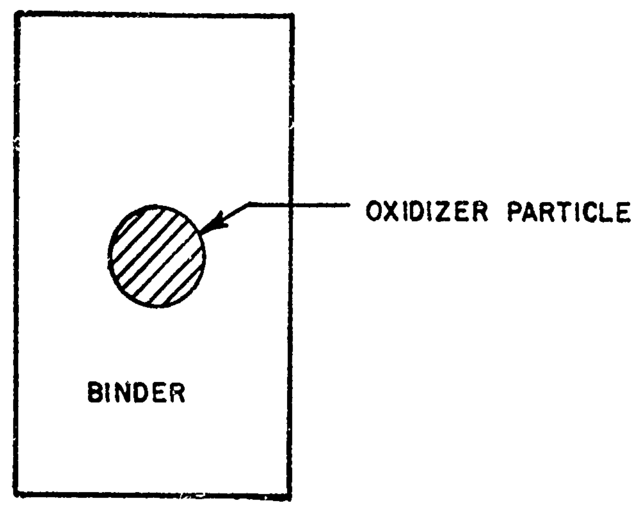


(a) Oxidizer particle held on propellant surface by acceleration forces ($F_b > F_d$)

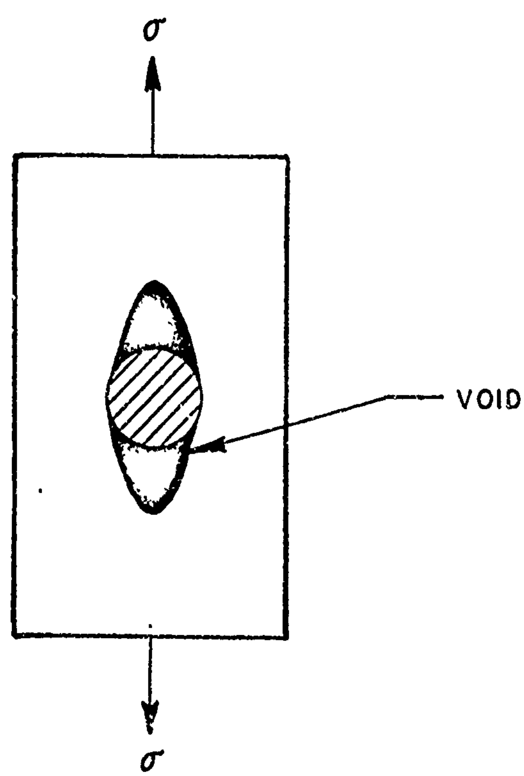


(b) Oxidizer particle carried away by aerodynamic drag forces ($F_d > F_b$)

Figure 3. Sturm's Model in an Acceleration Field



(a) as cast propellant



(b) dewetted propellant

Figure 4. Void Formation Upon Dewetting

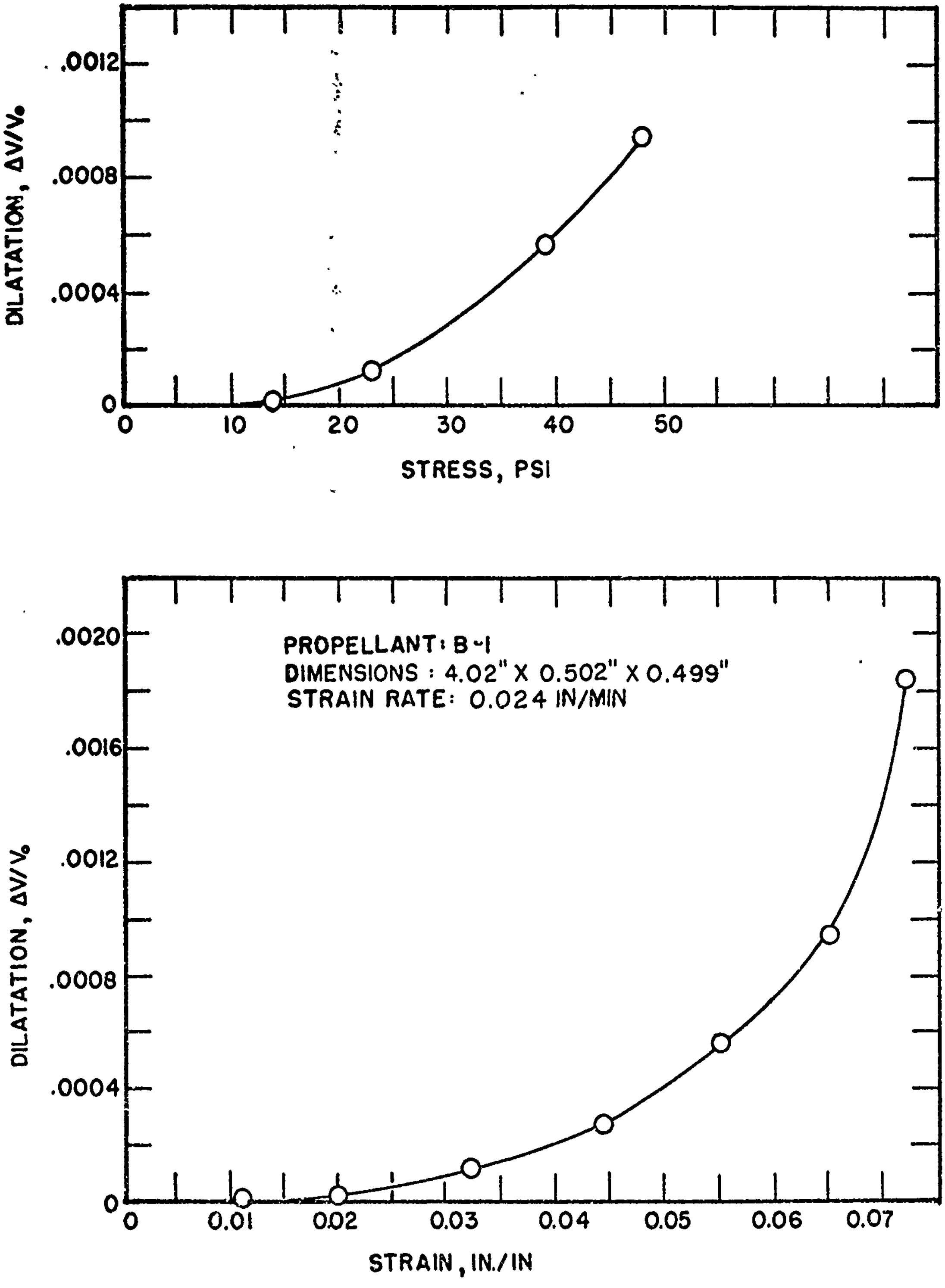


Figure 5. Dilatation versus Stress and Strain for Propellant B-1.

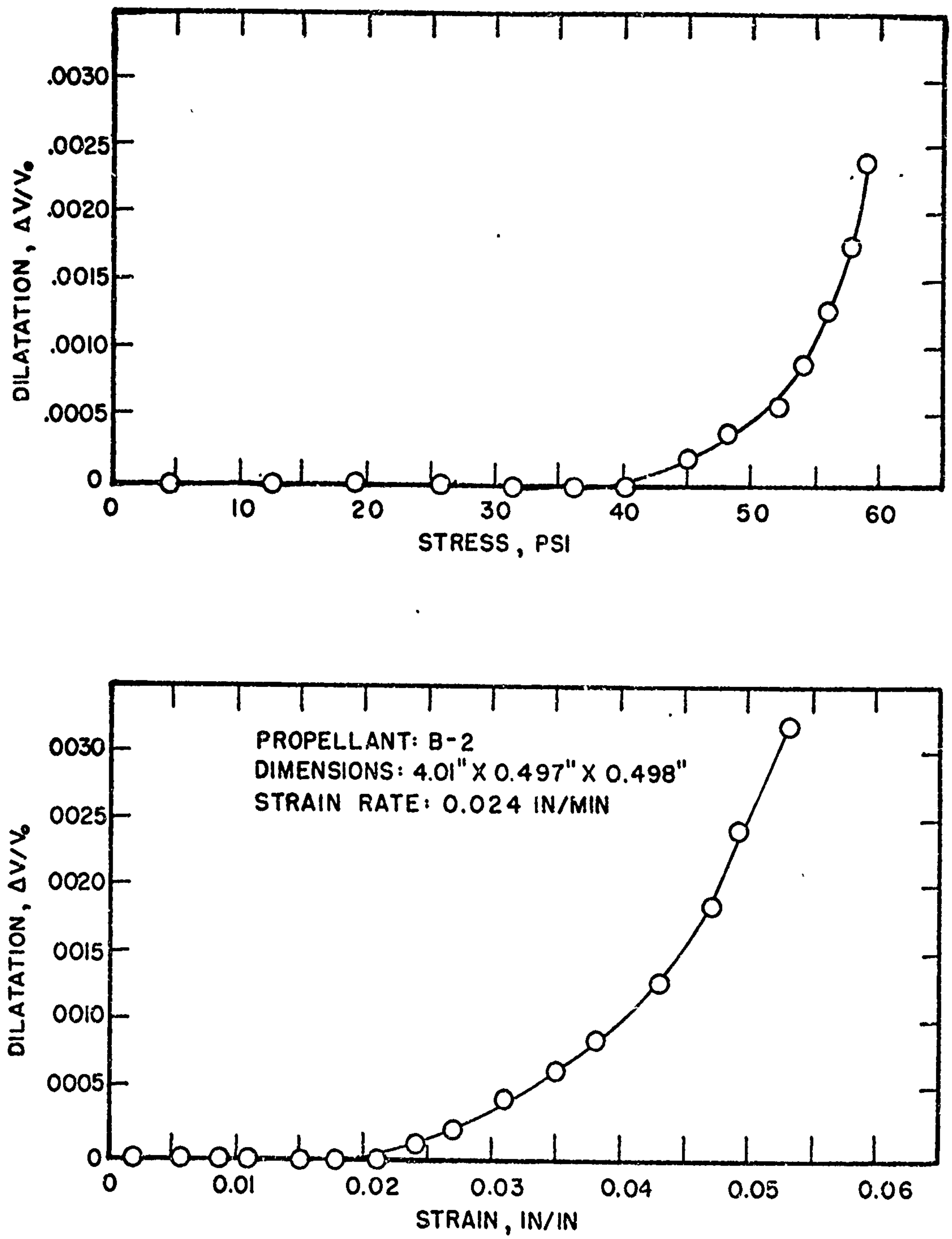


Figure 6. Dilatation versus Stress and Strain for Propellant B-2

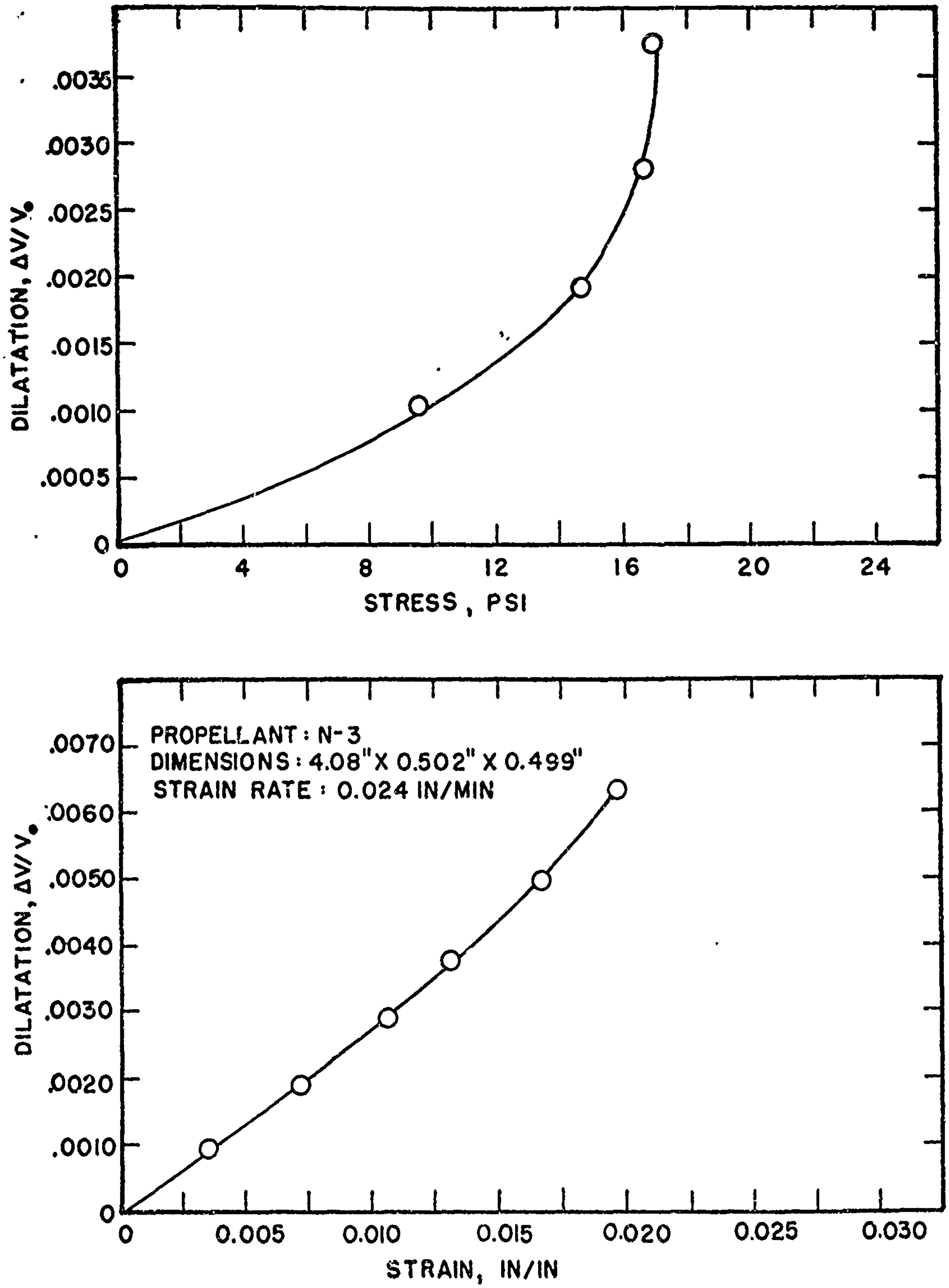


Figure 7. Dilatation versus Stress and Strain for Propellant N-3

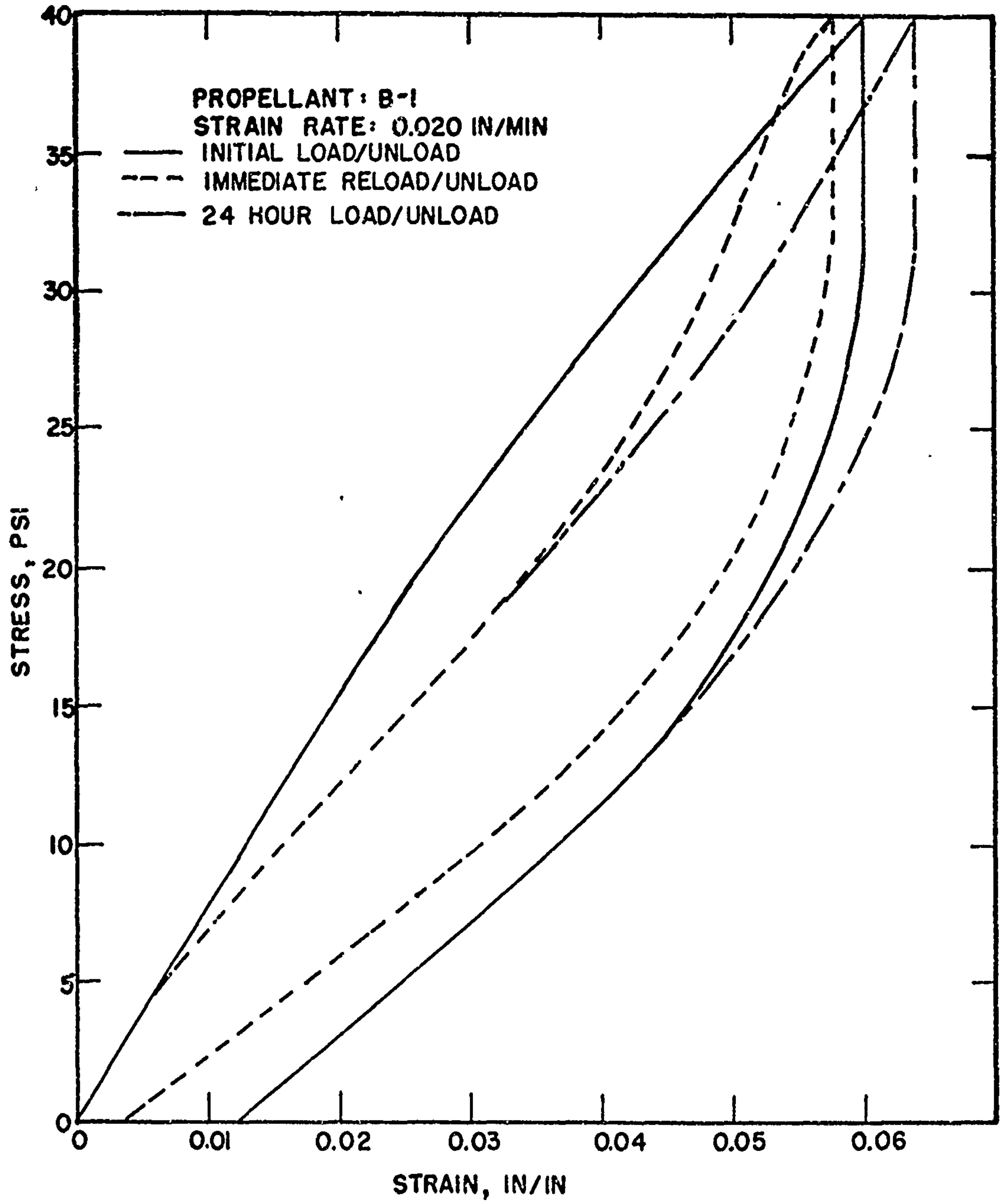


Figure 8. Stress versus Strain for propellant B-1

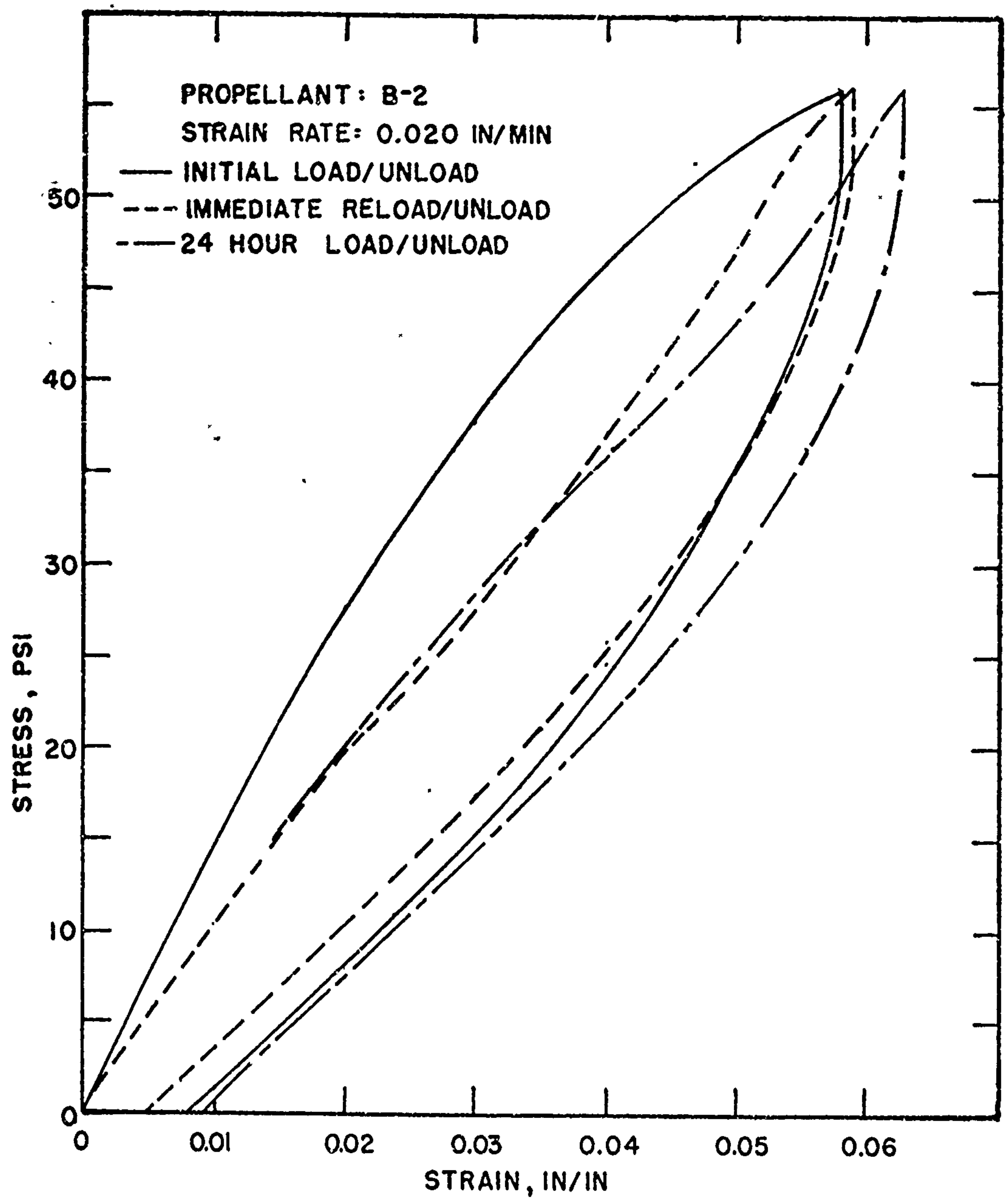


Figure 9. Stress versus Strain for Propellent B-2

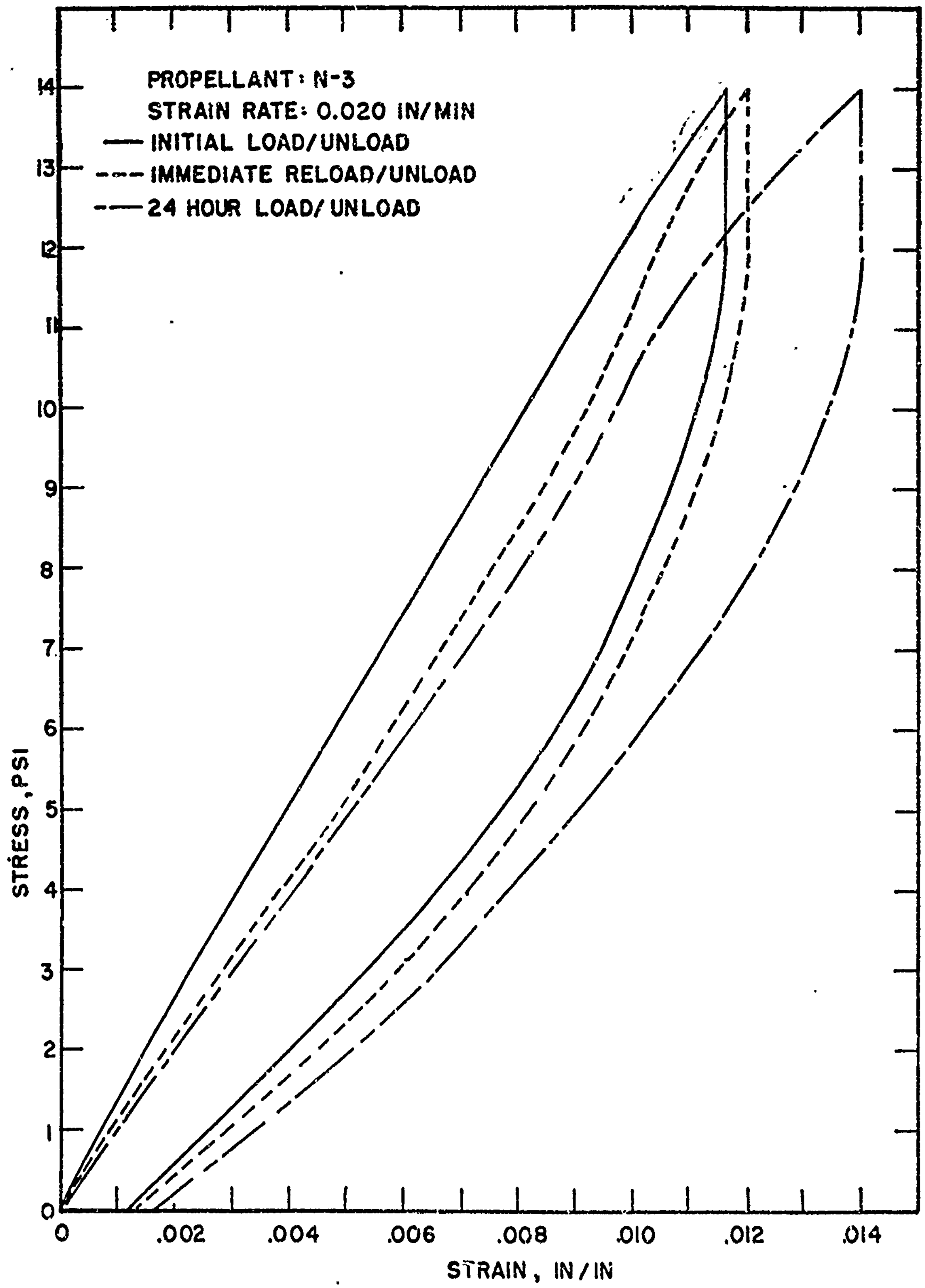


Figure 10. Stress versus Strain for Propellant N-3

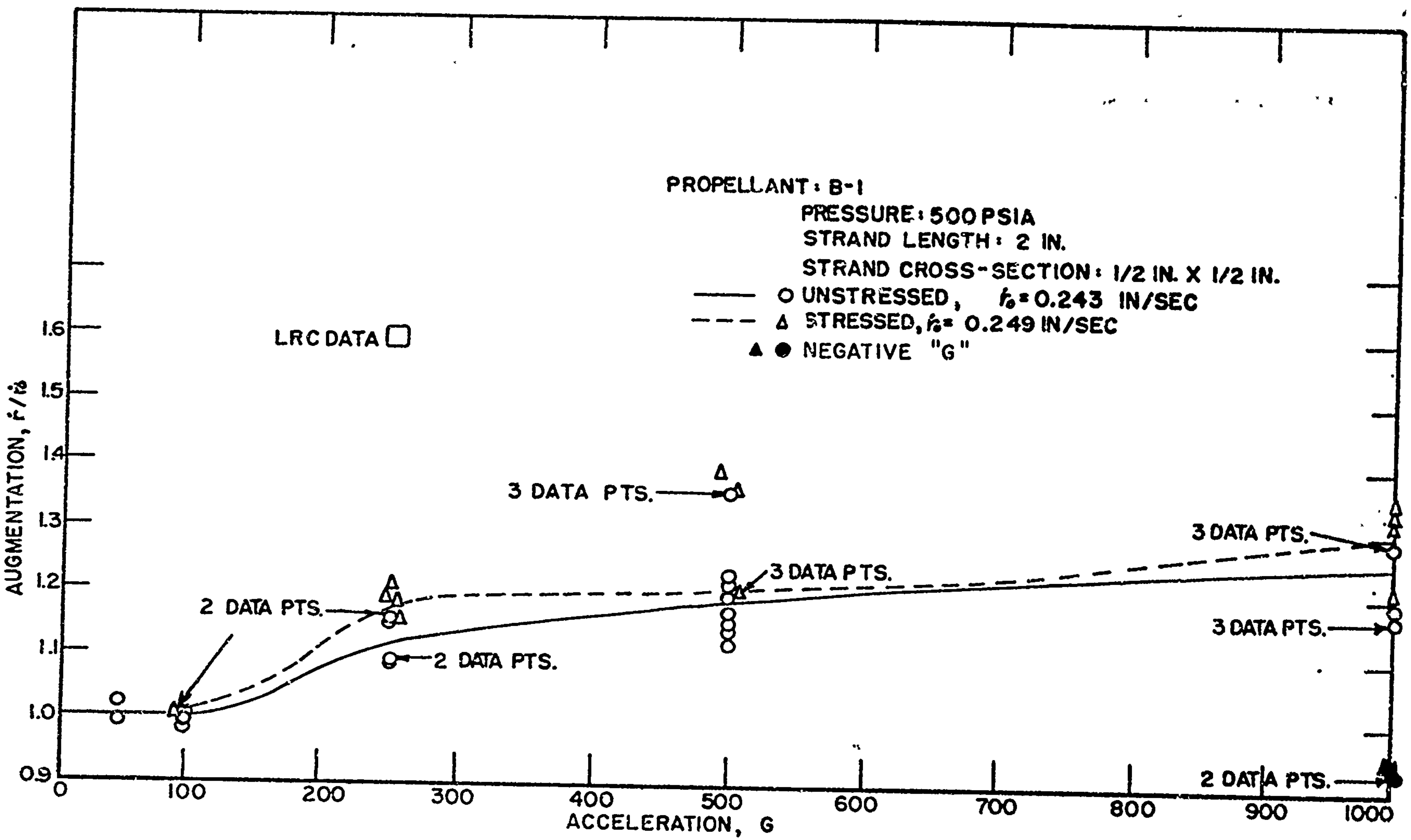


Figure 11. Augmetation versus Acceleration for Propellant B-1

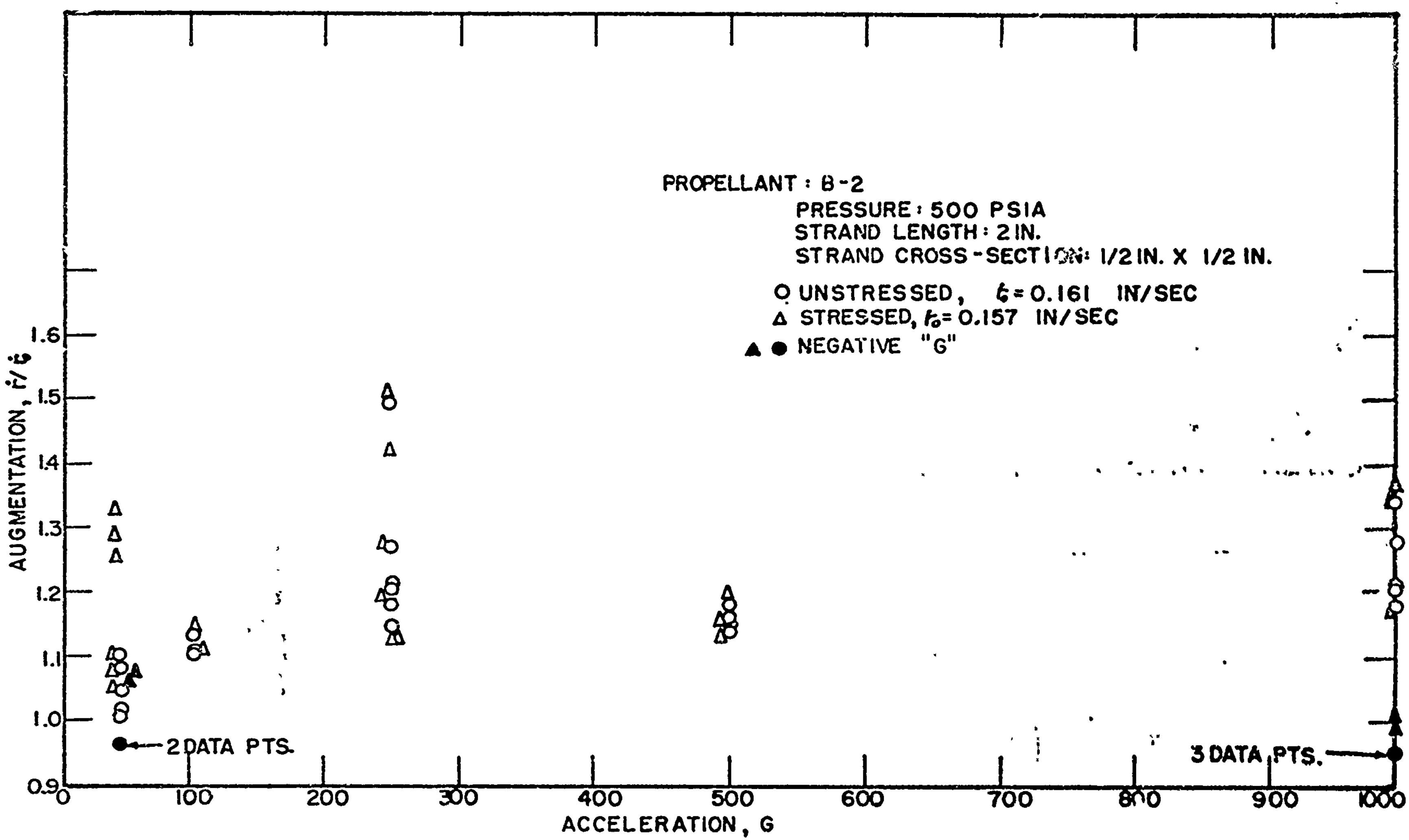


Figure 12. Augmentation versus Acceleration for Propellant B-2

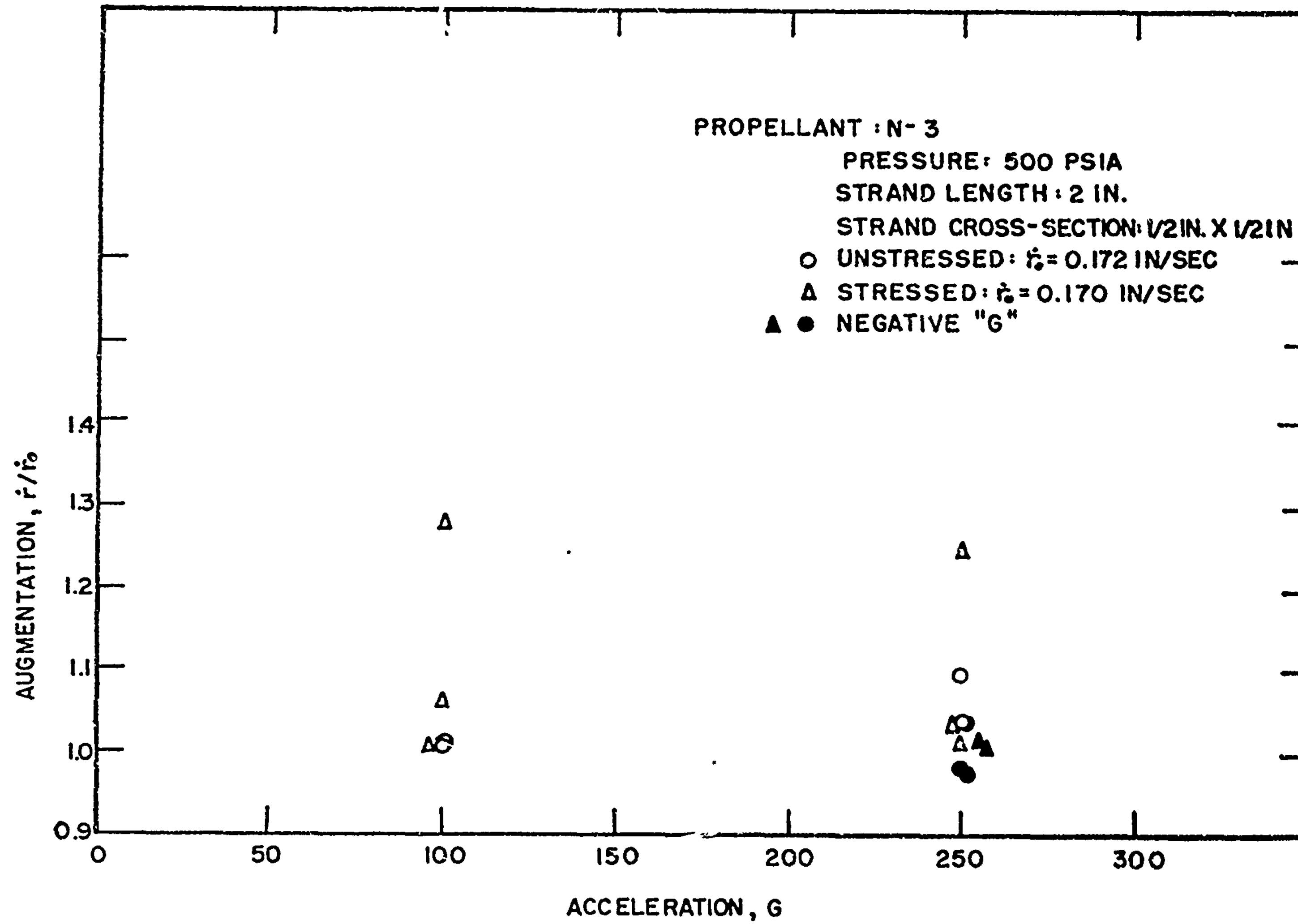


Figure 13. Augmentation versus Acceleration for Propellant N-3

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